Hydrogeological and Geochemical Approach in the Study of Groundwater Salinity of Central Haouz

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Abstract

This study aims to improve knowledge of the hydrogeology of the Haouz Central aquifer and to record a hydrochemical characterization of groundwater and surface water. The geological map of the area shows a basin deposited on a Palaeozoic basement, filled with the dismantling of the upper Atas and Jbillets, and crossed by outcrops of the Palaeozoic basement (Exp: Guemassas and Tazakourt).

On a hydrogeological level, groundwater circulation is geologically controlled and traces a flow to the northwest. The study area is drained by wadi Rhyghaya, wadi N’fiss and wadi Assif l’mal. The groundwater circulation is geologically controlled and traces a flow to the northwest.

The study of groundwater mineralization has shown the strong bond between it and chlorides, sulphates, calcium and sodium. It increases gradually from South to North, recording calcium saturation along the wadi Tensift. The study of strontium and sulphates proves the contribution of evaporitic rocks of Trias.

Keywords: Central Haouz, hydrochemistry, groundwater quality, Salinity.

1. Introduction
The world's water reserves are considerable about 1.4 billion km, of which only 3% is freshwater. It is distributed on less than 1% of groundwater and 0.01% on surface water (Marsily et al., 1995). Despite its scarcity, freshwater salinizes, by various processes either in an anthropic way through irrigation or
sometimes with natural phenomena such as salinization by dissolution or evaporation, as well as by mixing with Water Sea.

The first studies on water resources and salt water in Morocco were developed by Margat in 1961, and Carlier, 1971).

The Haouz Central is part of the plain of Haouz, which is located south of the hills of Jebilet and north of the High Atlas of Marrakech. This plain contains several groundwater layers, residing in different lithological formations (from Jurassic to Quaternary). Overexploitation and salinization are the major problems behind the change in the quality of these aquifers.

Previous studies have demonstrated the discontinuity of the hydrogeological and hydro-chemical character between the right and left bank of the wadi Tensift. A special feature of internal salinization is recorded at the Hercynian outcrops (Tazakourt, Sidi Mbarek). Thanks to the development of the mining works in the area, it has been possible to highlight the phenomenon of the salinization of the waters by crossing the deep ground.

In the light of the prospects of the works, this first work consists of characterizing the underground waters of the central Haouz, and studying the mineralization at the Hercynian outcrops.

2. Study Area Description

2.1. Geographic Location

The plain of Haouz located in the large Tensift, basin covers an area of 6000 km² (120 km long and 50 km wide). It’s bounded by the High Atlas to the south, by Jebilets to the north, by the middle Atlas to the east and the Ouled Boussebaa plateaux (Sidi Mokhtar plain) to the west (Fig. 1).

The study area is bounded on the north by wadi Tensift, on the east by wadi Ghmat, on the west by wadi Assif Elmal and on the south by the High Atlas of Marrakech. It is a quaternary filling basin with Hercynian points in the center (Guemmassa hills), to the north (Tazakourt hill). The flow of the aquifer is from south to north with a steep gradient near the outcrops of the Atlas, which weakened to wadi Tensift.

2.2. Climatology

The Tensift Basin was characterized by an arid to semi-arid climate with an oceanic influence near the coast. The Haouz was characterized by an arid to semi-arid continental climate, with average annual
rainfall of about 360 mm / year in the south of the plain and 200 mm / year in the north of the plain. The area is characterized by two periods. A wet period is from October to April and a dry period between May and September. Average temperatures can reach 39 ° C, which causes strong evaporation.

2.3. Geology

2.3.1. Lithology

The Haouz basin in Marrakesh is a syncline in which has accumulated important detrital formations, resulting from the dismantling of the High Atlas Mountains and the Jebilets hills (Ferrandini and Le Marrec 1982).

These formations were distributed, discordantly, on Hercynian subsoil outcropping in many places. The Mesozoic and Cenozoic formations only appear at the edge of the Atlas. They are gradually reduced to the north and cancelled at wadi Tensift.

According to Ambroggi & Thuille (1952) and Cochet (1962), the stratigraphic series of the Haouz is constituted from the bottom to top: Paleozoic bedrock, consisting of schists, sandstones and quartzites (6000 to 8000 m) with limestone in the Devonian.

- **Triassic** formations (1200 m) are characterized by dolerite flows at the top, clays, sandstones and red conglomerates with evaporitic deposits (gypsum and rock salt).
- **The lower Jurassic** (Lias) is composed of limestones and dolomitic limestones with continental red formations in the top (500 m). The Upper and Middle Jurassic consist of continental formations to the east becoming marine to the west (200 meters of limestone and clay).
- **The Cretaceous** is composed of three levels: green marls and gypsiiferous red clays (200 m) at the base, dolomitic limestone, marls and marno-limestone (100 m) in the middle, sandstone and marl (100 m) at the end.
- **The Eocene** consists of calcareous and phosphated sand with yellow marl levels (50 m). The summit is characterized by red and brown continental formations (200 m).
- **The Neogene** consists of fluviolacustrine pink sandstone-marls, lacustrine limestone and conglomerates mark.
- **The Villafranchien** is characterized by conglomerates, sandstone marls, and lacustrine limestones.
- **The quaternary** (50 m) consists of sands, gravel, silts with detrital formations consolidated of the terraces.

Paleozoic outcrops at the Draa Sfar and Hajjar mines consist of three series of which we cite: the volcano-sedimentary complex at the base, characterized by volcanic acidic rocks (Rhyolites and rhyodacite), surmounted by pyroclastic facies (Tuff, Lapilli -tuff) sometimes sedimentary for Draa Sfar (sand-stone). The median series consists of sulphide mineralization under several structures (massive, banded, disseminated), with a stok-werk zone for Hajjar. The summit series is formed by a sedimentary facies composed of calcarous mud-stones for Draa Sfar and sandstone, limestones in Hajjar.
2.3.2. Structuring

The geological and geophysical works (Ambroggi and Thuille, 1952) and (Sinan, 1986) in Haouz were able to subdivide the Haouz into three sectors:

- Eastern Haouz marked by compartments resulting from ENE-WSW faults.
- The central Haouz is characterized by three faults. The first is that of Tahannaout oriented N-S, raising the western compartment (Horst des Guemassas). The second is that of Assoufid oriented SW-NE north of the horsts of Guemassas. It raised the paleozoic basement in the south compartment (Horsts des Guemassas). The N'Fis fault is intersected between wadi N'fis and the intersection of the Assoufid fault with wadi Lбааja. It raised the NE compartment.
- The western Haouz shows basins separated by primary Mukhaden outcrops. This is the basin of Mejjar oriented E-O and the basin of Sidi Zouin between wadi N'fis and Koudiat Moukhaden.

The structuring of the Paleozoic basement in the region saves the different Hercynian and Atlas tectonic phases.
3. Methods and Materials
A sampling campaign of groundwater was carried out on 61 wells and 5 surface points covering the study area in April and Mai 2015. These water points were piezometrically surveyed, using a 200 m piezometric probe, a GPS and a topographic map.

In situ, the same water points were measured for temperature, electrical conductivity, Ph and dissolved oxygen.

Samples are placed in fully filled polyethylene containers. Reagents are added according to the types of elements to be analyzed.

4. Results and Discussions
4.1. Hydrogeology
The first monograph of the plain of Haouz was made in 1952 by Ambroggi and Thuille. It is later supplemented by the reports of Thuille (1957) and Cochet (1962). In 1975, Bernert was able to develop a mathematical model of the water table and estimate its water balance.

The research work of Moukhchane in 1983 and Sinani in 1986 present a synthesis of all geological, hydrogeological and geophysical data since the 1950s. Then, investigations have focused on all the hydrogeological aspects of the plain. In 2000, Sinani published a study on Haouz by combining GIS, geophysics and geostatistics. The vulnerability and the risk of pollution of the Haouz water table were studied by Lyakhlofi in 2001. In the same year, Razoki set up a database management system for the management of groundwater resources of the plain. In 2007, Abourida made a hydrogeological approach to the Haouz aquifer by remote sensing, isotopy, GIS and modeling. In 2010, El Goumi studied the structure of the plain using gravimetry. The application of the gravimetry on the eastern Haouz plain has gave similar results on the understanding of reservoir geometry and groundwater circulation (Rochdane, 2013).

The Haouz basin is separated into a shallow unconfined groundwater flow system and deep confined groundwater flow system.

A first deep reservoir of Jurassic, Cretaceous and Eocene is characterized by low productivity and very limited expansion. Its beveled end is located a few kilometers north of the Atlas.

A second reservoir of the Plio-Quaternary series consists of formations resulting from the dismantling of the atlasic chain. The free phreatic water is located between 4 and 70 m deep. It is the most productive in the region and the most exploited.

The structural complexity of these deposits is manifested by the extreme spatial variability of the hydraulic gradient and hydrodynamic parameters (Sinani, 1986).

The regional direction of groundwater flow is to north-west. The hydraulic gradient is very strong near the high atlas weakened towards the Oued Tensift.
The depth of groundwater varies between a minimum of 8 m and a maximum of 92 m at Amezmiz. Most of the sampled water points (60%) are less than 20 m deep. The shallow depths are located near the wadis. The great depths are in the regions of Sidi Abdellah Ghiat, Aït Imour and near the High Atlas (Fig. 4).

**Figure 3:** Piezometric map (April-Mai 2015)

**Figure 4:** Map of depths
4.2. Hydrochemistry

4.2.1. Statistical Analysis

The statistical analysis of the major elements showed the following:

An average conductivity of 1748 $\mu$S / cm varied between 10 190 $\mu$S / cm at Zaouiet-ech-Cherradi and 455 $\mu$S / cm at "Chwiter". A standard deviation of 1669 $\mu$S / cm was characterized by the variability of the conductivity.

Contents of chlorides and sodium were varied respectively between 2989 mg/l and 693.85 mg/l at Zaouiet-ech-Cherradi and 14 mg/l and 7.44 mg/l in DaourTaloumt. The average levels are 366 mg/l for chlorides and 121.18 mg/l for sodium. Standard deviation for chloride was 512 mg/l, and 131.8 mg/l for sodium.

The distribution of sulphates and magnesium followed the same configuration as the conductivity. The maximum values are respectively 1068 mg/l and 426.20 mg/l at Zaouiet-ech-Cherradi. The minimums are 15.40 mg/l and 11.58 mg/l respectively at Chwiter. The average levels of sulphate and magnesium are 152 mg/l and 51.22 mg/l, respectively. The standard deviations are 172 mg/l and 61.03 mg/l, respectively.

The distribution of bicarbonates is different. It varies between a maximum of 589.7 mg/l in the Ourika region and a minimum of 205.60 mg/l in Sidi Zouine. The average bicarbonate content is 321 mg/l with a standard deviation of 83 mg/l.

The nitrate contents are approximately 18.25 mg/l on average with a standard deviation of 14.85 mg/l. The maximum is in the Douar of Oukhrifene in the hills of Guemassas with a value of 71.93 mg/l and a minimum of 1.92 mg/l at Tahannout.

As for calcium, it indicates a maximum of 719.83 mg/l at Zaouiet-ech-Cherradi and a minimum of 20.24 mg/l at DouarTamgounssi. The average calcium content is 137.57 mg/l with a standard deviation of 141.39 mg/l.

Strontium recorded a maximum of 6.22 mg/l at Zaouiet-ech-Cherradi and a minimum of 0.13 mg/l at Chwiter. The average content is 0.77 mg/l with a standard deviation of 0.93 mg/l.

Lithium was not detected in all samples as 38% of the values are below 0.0024 mg/l. For the rest, lithium recorded an average content of 0.001 mg/l and a standard deviation of 0.0071 mg/l.

<table>
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<tr>
<th></th>
<th>Cond. (uS/cm)</th>
<th>Tem. (°C)</th>
<th>pH</th>
<th>Ca (mg/l)</th>
<th>K (mg/l)</th>
<th>Li (mg/l)</th>
<th>Mg (mg/l)</th>
<th>Na (mg/l)</th>
<th>Sr (mg/l)</th>
<th>[Cl—] (mg/l)</th>
<th>[NO3—] (mg/l)</th>
<th>[SO4 --] (mg/l)</th>
<th>HCO3— (mg/l)</th>
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</thead>
<tbody>
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<td>19.75</td>
<td>7.44</td>
<td>139.07</td>
<td>7.96</td>
<td>0.01</td>
<td>52.20</td>
<td>128.73</td>
<td>0.78</td>
<td>381.77</td>
<td>18.93</td>
<td>156.33</td>
<td>329.94</td>
</tr>
<tr>
<td>Minimum</td>
<td>455.00</td>
<td>16.20</td>
<td>6.29</td>
<td>20.24</td>
<td>2.59</td>
<td>0.00</td>
<td>11.58</td>
<td>7.44</td>
<td>0.15</td>
<td>13.90</td>
<td>1.92</td>
<td>15.40</td>
<td>192.30</td>
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<td>8.20</td>
<td>719.83</td>
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<td>0.03</td>
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<td>693.85</td>
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<td>140.72</td>
<td>5.82</td>
<td>0.01</td>
<td>60.79</td>
<td>138.07</td>
<td>0.92</td>
<td>515.53</td>
<td>15.27</td>
<td>172.47</td>
<td>92.19</td>
</tr>
</tbody>
</table>

4.2.2. Principal Component Analysis

The correlation matrix of the major elements showed (Tab. 1):

- A very strong positive correlation (+ 90%) between conductivity, calcium, magnesium, strontium and chlorides.
- A strong positive correlation (between 80% and 90%) between conductivity, sodium, sulphates.
- A moderately high correlation (between 60% and 70%) between strontium and lithium, and between magnesium and phosphorus
- A moderate correlation (50%) between potassium and nitrates.
4.2.3. Mineralization of Water

The percentages of the anions vary in the following ranges: 5% <Cl<76%, 4% <SO4<48%, 7% <HCO3<83%. The cations are distributed at intervals of 15% <Na<45%, 24% <Ca2+=<38%, 1% <Mg2<60%.

The major elements were projected on the Piper diagram (Fig. 6). It showed that the groundwater had a sodium-chloride facies in the North, a Bicarbonates-calcium facies in the South.
**Figure 6:** Projection of groundwaters and surface waters in Piper diagram

![Piper diagram](image)

4.2.4. Spatial Distribution of Major Ions

**Figure 7:** contour maps of major ions

![Contour maps](image)
4.2.5. Assessment of Water Quality for Irrigation

The sodium adsorption ratio (SAR) expresses the relative activity of sodium ions in exchange reactions in soils. This index allows the impact of water on irrigation, measures the relative concentration of sodium in relation to calcium and magnesium. It is defined by the equation:

$$\text{SAR} = \frac{[Na^+]}{\sqrt{[Ca^{2+}] + [Mg^{2+}]}}$$

The spatial distribution of SAR is characterized by a low to medium ratio in the center of the area, but increasing to north-east and southwest (Fig. 8).

**Figure 8**: Spatial distribution of the SAR index

The water quality of the wells and the surface was evaluated using the Wilcox diagram. This involves electrical conductivity and sodium contents. The projection of the samples in the Wilcox diagram showed the following classes (Fig. 9):

- **Excellent**: 22% of samples have this quality, including three surface samples. It is the wadi Assif Imal, wadi Ghighaya and wadi N'fis at the dam of Lalla Takerkoust. For groundwater, this quality is limited in the southern part of the study area.
- **Good**: 51% of the waters sampled are good. It is distributed throughout the study area.
- **Admissible**: this quality is presented by 4% of samples. It is located in the Southeast of the sector.
- **Law**: 12% of samples represent this quality, including one surface sample (wadi Tensift)
- **Bad**: 10% of samples including two surface samples (wadi Tensift).
4.2.6. Studies of Metallic Trace Elements

Contamination of soils, atmosphere, hydrosphere and sediments by metallic trace elements (MET) is a major environmental problem. These elements are natural (alteration of the rocks, volcanism, erosion ...) but they are also derived from anthropic activities.

The following tables summarize the results of analysis of trace metals in groundwater and the surface water.

**Table 3:** Summary of METs in groundwater

<table>
<thead>
<tr>
<th>MET</th>
<th>Min ppm</th>
<th>Max ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
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<tr>
<td>Fe</td>
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<tr>
<td>Zn</td>
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<td>1.9779</td>
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<td>Se</td>
<td>&lt;0.0570</td>
<td>&lt;0.0570</td>
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<tr>
<td>Co</td>
<td>&lt;0.0100</td>
<td>&lt;0.0100</td>
</tr>
<tr>
<td>Mn</td>
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</tr>
<tr>
<td>Mo</td>
<td>&lt;1.9280</td>
<td>&lt;1.9280</td>
</tr>
<tr>
<td>B</td>
<td>&lt;0.0030</td>
<td>0.3613</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MET</th>
<th>Min ppm</th>
<th>Max ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>&lt;0.0210</td>
<td>&lt;0.0210</td>
</tr>
<tr>
<td>Cr</td>
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<tr>
<td>F</td>
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<td>&lt;0.0100</td>
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<td>Pb</td>
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<tr>
<td>Hg</td>
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<tr>
<td>Cd</td>
<td>&lt;0.0040</td>
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</table>

**Table 4:** Summary of METs in surface waters

<table>
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<tr>
<th>MET</th>
<th>Min ppm</th>
<th>Max ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>&lt;0.0036</td>
<td>&lt;0.0036</td>
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<tr>
<td>Fe</td>
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<th>MET</th>
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<tr>
<td>Cd</td>
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4.3. Origin of Salinity

4.3.1. Ratios Method

Chloride is a conserved element that does not participate in water-rock interactions. It constitutes a mixing tracer and characterizes the origin of the salinity of the waters. The major elements were compared to the fresh-water_salt-water mixing line.

- The relation between Ca$^{2+}$ and Cl$^-$ (Fig. 10 A) illustrates that all points are above the mixing line. This enrichment may be due to the interaction between water and carbonate rocks.
- The Na$^+$/Cl$^-$ graph (Fig. 10. B) shows that the majority of points are below the mixing line. The release of Na$^+$ is often explained by the basic ion-exchange phenomenon between water and the aquifer and resulting in an adsorption of Na$^+$ and Ca$^{2+}$ release. This is confirmed by the enrichment in Ca$^{2+}$ (Fig. 10 A).
- The relation between SO$_4^{2-}$ and Cl$^-$ (Fig. 10. C) shows that it is a sulphate enrichment. It indicates the presence of evaporitic rocks or agricultural contamination.
- The graph Mg$^{2+}$/Cl$^-$ (Fig. 10. D) also shows an enrichment in Mg$^{2+}$. It can be explained by the dissolution of dolomite.
- The Sr$^{2+}$/Cl$^-$ graph (Fig. 10. E) shows a slight strontium enrichment, which may be due to the dissolution of the celestite contained in the gypsiferous rocks.
- The Li$^{2+}$/Cl$^-$ graph (Fig. 10. F) shows lithium enrichment, evidencing the dissolution of evaporitic rocks as showed in the SO$_4^{2-}$/Cl$^-$ graph.
4.3.2. Ratio Mg$^{2+}$/Ca$^{2+}$

The evolution of the Mg$^{2+}$/Ca$^{2+}$ ratio depends mainly on the interactions between the rock and the water which can lead to dolomitization, dissolution and precipitation.

The Ca$^{2+}$-Mg$^{2+}$ exchange reaction, dolomitization, is reported as the main cause of the decrease in the Mg$^{2+}$/Ca$^{2+}$ ratio in the waters of carbonate basins. This reduction is progressive in ascending age of aquifers and controlled by the balance calcite-dolomite and temperature (Fidelibus et al. 1996). The reduction of Sulphate favors the dissolution of carbonate minerals. This could change the Mg$^{2+}$/Ca$^{2+}$ ratio.

Mg$^{2+}$/Ca$^{2+}$ graph shows a mean correlation (75%) between these two elements. it traces a slight slope towards the Ca$^{2+}$ axis (Fig. 13). Enrichment in Mg$^{2+}$ is observed at a few points south-west of the study area (Fig. 12).
4.3.3. Characterization of Strontium
Strontium is always related to evaporites. High levels of Sr$^{2+}$ in water can only be explained by the dissolution of celestite (SrSO$_4$), a mineral associated with gypsum. Strontium is a good marker for detecting the presence of evaporites (Carre, 1975).

Strontium levels in the groundwater of central Haouz range from 0.13 to 6.22 mg/l. Strontium allows distinguishes sulfates resulting from sulphide oxidation (low levels) from those resulting from the dissolution of evaporites (high levels).

The Sr$^{2+}$/Ca$^{2+}$ ratio is characteristic of an evaporitic origin if it is equal to or greater than 1‰ (Bakalowicz, 1984). It is greater than 5 in the alpine Triassic evaporites (Meybeck, 1984).

The ratio of Sr$^{2+}$/Ca$^{2+}$ map (Fig. 13) summarizes its distribution in the study area. The values are greater than 1‰, and distinguish two main groups:

A group of less than 5‰: located mainly in the center of the area.

A group greater than 5‰: located near the high atlas, on the massif of Guemassas and north-west near the wadi Tensift.

This configuration perfectly coincides with the spatial distribution of sulphates which shows the same groups (Fig. 7).
4.3.4. Saturation Index
Super-saturation in calcite, dolomite and aragonite has been demonstrated by calculating the saturation index. It is expressed in 28% of the calcite samples, in 21% of the dolomite samples and 15% of the aragonite samples.

This indicates that only the carbonate minerals tend to precipitate, especially in dolomitic form. In addition, the evaporitic minerals are always in the state of under saturation (Fig. 14).

Figure 13: Sr²⁺/Ca²⁺ ratio distribution map

Figure 14: variation of saturation indices
5. Conclusion
This first hydro-chemical characterization of the central Haouz has shown that the depth of the water table groundwater varies between 5.5m and 92m with a flow going from South-East to North-West. This area is characterized by an electrical conductivity average of 2419 uS / cm but with a very high standard deviation 1830 uS / cm between a maximum of 10190 uS / cm and a minimum of 483 uS / cm.

The mineralization of the water is controlled by the anions of $\text{HCO}_3^-> \text{Cl}-> \text{SO}_4^{2-}$ and the $\text{Ca}^{2+}> \text{Na}^+ > \text{Mg}^{2+}$ cations, and increases from south to north of the basin. Groundwater contains a variety of hydro-chemical facies, known as sodium chloride, calcium chloride, sodium bicarbonate and calcium bicarbonate facies.

The analysis of the mineralization has shown that the latter is related to the presence of evaporitic rocks, demonstrated by the study of the major elements and by the study of strontium ($\text{Sr}^{2+} / \text{Ca}^{2+}$ ratio). The concentration of strontium compared to that of sulphates traces the same spatial configuration (see 4th and 11th Figures). In the same way, the study of calcium and magnesium combined with the saturation indices showed the enrichment of calcium and magnesium, which reaches the precipitation stage in the form of calcite, aragonite and dolomite (Fig. 13).

The majority of groundwater samples in the area are good for irrigation. In addition, the contamination of waters by the MTEs is not pronounced in the zone.

This preliminary study will be complemented by a detailed geological study of the central Haouz basin and an isotopic outlet to better understand the problem of general and point salinization.

Bibliographie


